Electrochimica Acta 180 (2015) 173–177

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Heat-treated 3,5-diamino-1,2,4-triazole/graphene hybrid functions as an oxygen reduction electrocatalyst with high activity and stability

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ARTICLE INFO

Article history:
Received 10 June 2015
Received in revised form 18 August 2015
Accepted 21 August 2015
Available online 28 August 2015

Keywords:
Copper
Electrocatalyst
Graphene
Nitrogen
Oxygen reduction

ABSTRACT

We synthesized a novel copper-based oxygen reduction electrocatalyst by heat treating a mixture of reduced graphene oxides and a copper complex of 3,5-diamino-1,2,4-triazole at 900 °C for only 45 s. Extended X-ray absorption fine structure and X-ray photoelectron spectroscopy analyses of the synthesized catalyst revealed that the nitrogen (N) atoms coordinated to copper (Cu) atoms were doped into the *sp2*networks of graphene. In neutral solutions, the catalyst exhibited efficient electrocatalytic activity for oxygen reduction, with an onset potential of 790 mV. More importantly, the catalyst possesses high stability due to the anchoring of active Cu-sites into the graphene substrate via the Cu-N coordination bonds.

1. Introduction

The electrochemical oxygen reduction reaction (ORR) occurs at the cathode side of various types of fuel cells. Although hydrogen-oxygen fuel cells generally operate under acid or alkaline conditions, the ORR in neutral solutions has also attracted much attention for application in enzymatic and microbial fuel cells [1–4]. At present, platinum (Pt) is generally used as the cathode electrocatalyst for accelerating the ORR. However, as Pt is expensive due to its scarcity, the use of earth-abundant materials as catalysts is considered to be an essential requirement for the further dissemination of biofuel cells. One promising strategy to develop cost-effective catalysts is to learn from natural systems. In living cells, copper (Cu)-containing enzymes, such as laccase and bilirubin oxidase, catalyze the four-electron ORR for respiration with lower overpotential than Pt in neutral pH conditions [1–3]. In these enzymes, modulation of the electronic state of the central Cu by coordination with nitrogen (N) atoms is believed to be a key factor for the high catalytic activity [5,6]. For this reason, numerous studies have described the synthesis of Cu-based complexes with N-ligation that mimic Cu-enzymes [7–13]. For example, a dinuclear Cu complex of 3,5-diamino-1,2,4-triazole (Cu-DAT) supported on carbon black exhibited an onset potential of 0.73 V (vs. RHE) at pH 7 for the ORR, which is the highest value among Cu-based catalysts reported to date [8,14]. In addition, Cu-DAT also served as the cathode catalyst in alkaline fuel cells [15]. Although Cu-DAT is therefore a promising platform for the development of low-cost ORR catalysts, its half-wave potential for the ORR decreased by about 140 mV after 100 cycles of cyclic voltammograms (CVs) [8]. Thus, for the practical application of this catalyst, it is necessary to improve its stability.

Carbon-based materials containing N and metals, such as iron (Fe) and/or cobalt (Co), are alternative candidates as ORR electrocatalysts because the stability of these catalysts is much improved compared to that of molecular catalysts [16–21]. We recently reported that stable graphene materials with Fe-N coordination bonds can be synthesized by the short-duration heat treatment (<60 s) of graphene oxides in the presence of an Fe–pentaethylenehexamine complex [22,23]. Notably, the use of the short-duration heat treatment improved the stability of the prepared catalyst while maintaining Fe-N coordination. For this reason, it is worth investigating whether this synthesis method can be applied to Cu-DAT, which exhibits the highest performance among Cu-based complexes [8].

2. Experimental

2.1. Materials

Reduced graphene oxides (r-GOs) were synthesized through the heat treatment (900 °C) of graphene oxides under an inert atmosphere, as detailed in our previous report [24]. It should be noted here that no metal residue was observed in the resulting r-GOs from X-ray photoelectron spectra. $CuCl_2 \cdot 2H_2O$ (114 mg; Wako)

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http://dx.doi.org/10.1016/j.electacta.2015.08.120
0013-4686/

and 3,5-diamino-1,2,4-triazole (132 mg; TCI) were dissolved in 10 ml ultra pure water to form Cu-DAT complex in solution. A total of 200 mg r-GOs was added to 9.14 ml of the Cu-containing aqueous solution, and the resulting mixture was dried. The obtained material was placed at the bottom of a half-closed quartz tube filled with argon and quickly inserted into a muffle furnace preheated to 900 °C. After heat treatment for 45 s, the tube was quickly removed from the furnace and immediately cooled under argon flow. The synthesized material was washed with 2 M H_2SO_4 at 60 °C for 3 h. The resulting catalyst was designated HT/Cu-DAT (HT: Heat treatment). The Cu-DAT complex supported on r-GOs (non-HT/Cu-DAT) was prepared on the basis of previous paper [8], except for the use of r-GOs as carbon supports. 20wt% Pt/C (Fuel Cell Earth) was also used as a reference sample.

2.2. Electrochemical measurements.

Oxygen reduction activities were evaluated using a rotating ring-disk electrode (RRDE) in a 0.1 M phosphate-buffer solution containing 0.5 M $NaClO_4$ (pH 7.0). The counter electrode was a titanium wire. A Ag/AgCl/KCl sat. was used as the reference electrode and was calibrated with respect to a reversible hydrogen electrode (RHE = Ag/AgCl/KCl sat. + 0.198 V + 0.0591 × pH at 25 °C). Working electrodes were first prepared by dispersing 5 mg of each catalyst in 437.5 μl ethanol and 47.5 μl of 5 wt% Nafion solution (Aldrich). The resulting catalyst inks were dropped in 2.5-μl aliquots onto a glassy carbon electrode (0.196 cm^2). Therefore, the amounts of loaded catalyst and Nafion were controlled to be approximately 0.13 $mg \cdot cm^{-2}$ and 0.06 $mg \cdot cm^{-2}$, respectively.

The number of electrons was evaluated by using a RRDE and calculated based on the Eq. (1) [22].

$$n = 4Id/(Id + Ir/N) \quad (1)$$

in which N (= 0.41), Id and Ir are the collection efficiency, disk current and ring current, respectively. The poisoned potential on the Pt ring was 1.2 V versus RHE. We also estimated the number of electrons from the Koutecky-Levich equation as follows:

$$j^{-1} = \omega jk^{-1} + (B\omega^{1/2})^{-1} \quad (2)$$

where j is the measured current, j_k is the kinetic-limiting current and ω is the electrode rotation rate. The theoretical value of the Levich slope (B) was evaluated from the following relationship:

$$B = 0.62nFCD2^{/3}\nu^{-1/6} \quad (3)$$

where n is the number of electrons, F is the Faradic constant (96485C mol^{-1}), C is the bulk concentration of oxygen (1.13×10^{-6} mol cm^{-1}), D is the diffusion coefficient of oxygen (1.8×10^{-5} cm^2 s^{-1}), and ν is the viscosity of the electrolyte (0.01 cm^2 s^{-1}).

The stability of catalysts was also evaluated using a rotating disk electrode (RDE). Rotation speed and scan rate were set at 1500 rpm and 250 mV s^{-1}, respectively, during 1000CVs.

2.3. X-ray measurements.

Hard X-ray absorption measurements (XAFS) were performed using the hard X-ray beam line 01B01 at SPring-8, Japan. Transmission yield spectra were acquired using a double-crystal Si (111) monochrometer. X-ray photoelectron spectroscopy (XPS) analyses (Axis Ultra, Kratos Analytical Co.) were obtained using monochromated Al Kα X-rays at hν = 1486.6 eV.

3. Results and discussion

Cu K-edge extended X-ray absorption fine structure (EXAFS) analyses were first conducted to confirm that Cu-N coordination bonds remained in HT/Cu-DAT. Fig. 1 shows the Fourier transformation of k^3-weighted EXAFS oscillation for HT/Cu-DAT, Cu phthalocyanine and Cu foil. The EXAFS spectra for HT/Cu-DAT and Cu phthalocyanine displayed peaks derived from the first coordination sphere at R = 1.43 Å and 1.50 Å, respectively, which were assignable to Cu-N bonds. The coordination number for N atoms was estimated to be 1.7 in HT/Cu-DAT. Cu foil had a peak corresponding to the first coordination sphere at R = 2.16 Å, which was ascribed to Cu-Cu bonds. Importantly, this peak was not observed for HT/Cu-DAT. In contrast, the EXAFS spectrum for the heat treated sample without the acid treatment (Fig. S1) shows both the Cu-N and Cu-Cu peaks. These results indicate that a

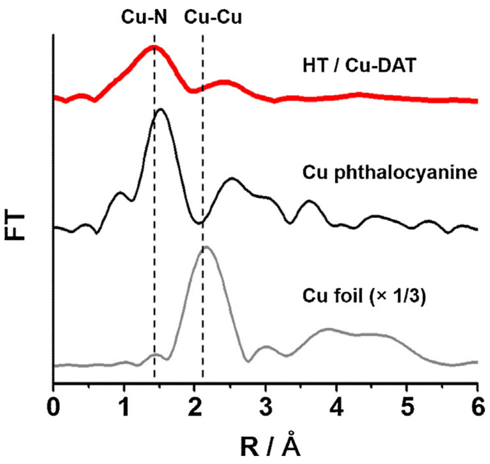

Fig.1. Fourier transformation (FT) of k^{3}-weighted EXAFS oscillation for heat-treated (HT)/Cu-DAT after the acid treatment (red), Cu phthalocyanine (black) and Cu foil (gray).

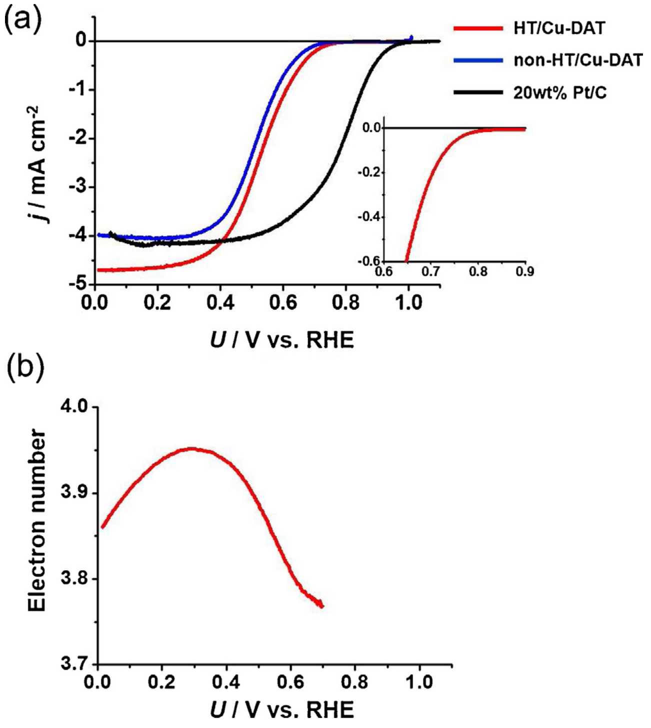

Fig.2. (a) j vs. U curves for HT/Cu-DAT (red) and non-HT/Cu-DAT (blue) in 0.1 M phosphate buffer solution (pH = 7.0). The inset shows the magnified curve for HT/Cu-DAT. These curves were obtained by subtracting the cyclic voltammetries (CVs) in argon-saturated electrolyte solution from those obtained in O_2-saturated electrolyte solution. (b) Electron number for HT/Cu-DAT. Rotation rate: 1500 rpm; scan rate: 10 mV s^{-1}.